DALTON
FULL PAPER

Synthesis and characterisation of the first unidimensional cobalt hydrogen phosphate, $[H_3N(CH_2)_3NH_3][Co(HPO_4)_2]$

Andrew R. Cowley and Ann M. Chippindale *

Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford, UK OX1 3PD

Received 22nd February 1999, Accepted 19th May 1999

The first unidimensional organically templated cobalt hydrogenphosphate, $[H_3N(CH_2)_3NH_3][Co(HPO_4)_2]$, has been synthesized at 433 K under solvothermal conditions in the presence of 1,3-diaminopropane and the structure determined at 150 K using single-crystal X-ray diffraction. The compound contains anionic chains of formula $[Co(HPO_4)_2]^{2-}$ constructed from edge-sharing 4-membered rings of alternating CoO_4 and HPO_4 tetrahedra from which hang additional "pendant" HPO_4 groups. The chains, which are structurally similar to those found recently in unidimensional aluminophosphates, are held together by a network of hydrogen bonds involving both interchain and chain–diamine interactions.

Introduction

The considerable interest shown recently in the synthesis and characterisation of open-framework metal phosphates reflects their potential applications as molecular sieves, ion-exchange materials and heterogeneous catalysts. The use of organic amines in phosphate synthesis has led to a plethora of new materials with either 3- or lower-dimensional structures. The structure-directing properties of these amines are not as yet well understood and use of one amine can lead to the formation of a number of different framework structures. This is clearly illustrated by 1,3-diaminopropane, which may form 3-dimensional structures including $[H_2N(CH_2)_3NH_3][HAl_3P_3O_{14}]\cdot H_2O$,[1] $[H_3N(CH_2)_3NH_3][(VO)_3(OH)_2(H_2O)_2(PO_4)_2]$[2] and $[H_3N(CH_2)_3NH_3]_2[Fe_4(OH)_3(HPO_4)_2(PO_4)_3]\cdot xH_2O$,[3] 2-dimensional structures such as $[H_3N(CH_2)_3NH_3]_{0.5}[VO][VO_4]$[4] and $[H_3N(CH_2)_3NH_3]_{0.5}[Co(PO_4)]\cdot 0.5H_2O$[5] or unidimensional chain structures such as $[H_3N(CH_2)_3NH_3][Ga(HPO_4)(PO_4)]$.[6] In this paper we describe the use of 1,3-diaminopropane in the synthesis of the first organically templated unidimensional cobalt hydrogenphosphate, and the structural characterisation of this material using single-crystal X-ray diffraction.

Experimental

The compound $[H_3N(CH_2)_3NH_3][Co(HPO_4)_2]$ was prepared under predominantly non-aqueous solvothermal conditions. The oxide CoO (0.4 g) was suspended in ethylene glycol (6 cm^3) by stirring and 1,3-diaminopropane (1.5 cm^3) added to act as structure-directing agent. The mixture was stirred until homogeneous and then aqueous H_3PO_4 (1.5 cm^3, 85% by weight) added with further stirring to give a gel of overall composition $CoO : 20\,HOC_2H_4OH : 3.4\,H_2N(CH_2)_3NH_2 : 4.1\,H_3PO_4 : 3.9\,H_2O$. The gel was placed in a Teflon-lined stainless-steel autoclave and heated at 433 K for 7 d. The resulting solid product consisted of a biphasic mixture of deep-blue needles of the $[H_3N(CH_2)_3NH_3][Co(HPO_4)_2]$ and colourless blocks. The latter were identified by single-crystal X-ray diffraction as the diammonium hydrogenphosphate hydrate $[H_3N(CH_2)_3NH_3][HPO_4]\cdot H_2O$[7] (monoclinic, space group $P2_1/c$, lattice parameters $a = 6.9808(8)$, $b = 16.724(1)$, $c = 7.8550(7)$ Å, $\beta = 113.657(9)°$ at 200 K). The solid was washed with 3 × 20 cm^3 glacial acetic acid and 3 × 20 cm^3 methanol to remove the diammonium hydrogenphosphate hydrate and dried in air at 344 K. The resulting product was shown by powder X-ray diffraction (Fig. 1) to be monophasic. Combustion analysis results are C 10.78, H 4.70 and N 8.29% by weight, which are in good agreement with the values of C 11.02%, H 4.31% and N 8.57% calculated for the formula $[H_3N(CH_2)_3NH_3][Co(HPO_4)_2]$. Although stable indefinitely in dry air, a finely ground sample of the compound reacted rapidly with water at room temperature to form a pale-pink gelatinous solid which was shown to be amorphous by powder X-ray diffraction.

An infrared spectrum of the compound (Perkin-Elmer 1710 FT spectrophotometer, KBr disc) showed a broad, strong absorption band in the range 3600–2300 cm^{-1} and a number of sharp, medium-intensity bands in the range 1670–1170 cm^{-1}. Bands in the former region are compatible with OH, NH and CH stretching modes and in the latter with NH_3, CH_2 and OH deformation modes, consistent with the presence of $H_3N(CH_2)_3NH_3^{2+}$ and OH groups.

A single crystal suitable for X-ray diffraction study (size 0.06 × 0.12 × 0.40 mm) was selected from the as-synthesized material and mounted on a nylon fibre using a drop of perfluoropolyether oil. It was then rapidly cooled to 150 K in a flow of cold nitrogen using an Oxford Cryosystems CRYOSTREAM cooling system. Data were collected on an Enraf-Nonius DIP2020 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Images were processed using the DENZO and SCALEPACK suite of programs.[8] Data were corrected for Lorentz and polarisation effects and a partial absorption correction applied by multiframe scaling of the image-plate data using equivalent reflections. The systematic absences in the data ($h00$, h odd; $0k0$, k odd; $00l$, l odd) indicated the space group to be $P2_12_12_1$. 2030 Unique reflections were measured of which 1721 were observed with $I > 3\sigma(I)$. Full experimental information is given in Table 1.

The structure was solved using direct methods (SIR92)[9] and all non-hydrogen atoms located. Framework hydrogen atoms were subsequently located in Fourier-difference maps and the hydrogen atoms of the diamine placed geometrically after each cycle of refinement. Full-matrix least-squares refinement on F of 153 parameters (atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms, atomic coordinates only of hydroxyl hydrogen atoms) was carried out using the program CRYSTALS.[10] A Chebychev 3-term polynomial weighting scheme was applied. The final residual electron densities were -0.789 and 0.671 e $Å^{-3}$. The crystal was found to be a racemic

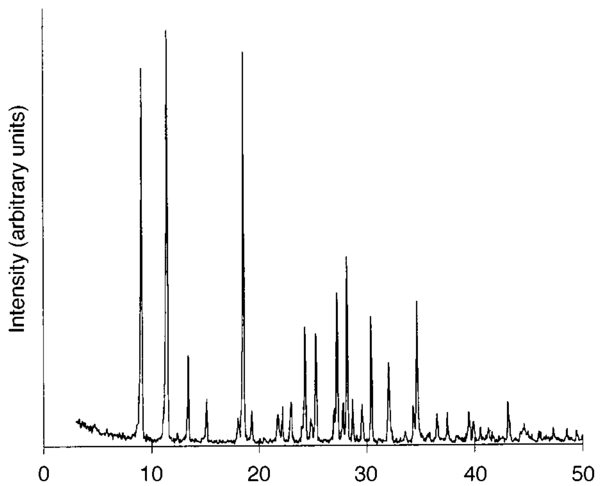

Fig. 1 Powder X-ray diffraction pattern of a finely ground sample of the compound (Philips PW1700 diffractometer, graphite-monochromated Cu-Kα radiation).

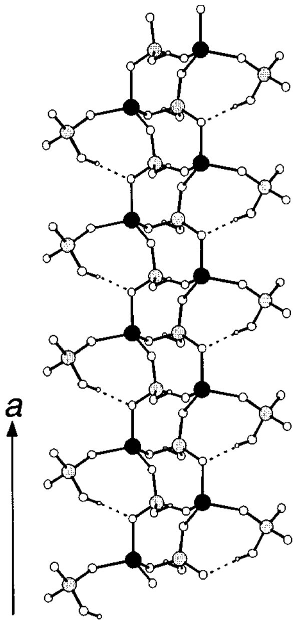

Fig. 2 View of one polymeric anion of the compound along the vector [011], showing zigzag chains of four-membered rings built from CoO_4 and $HP(1)O_4$ tetrahedra linked to pendant $HP(2)O_4$ groups. Intra-chain hydrogen bonds are shown as dotted lines. Key: black circles, Co; grey circles, P; large white circles, O; small white circles, H. Drawing package ATOMS.[12]

twin with twin ratio *ca.* 50%. Selected bond lengths and angles are given in Table 2.

CCDC reference number 186/1474.

See http://www.rsc.org/suppdata/dt/1999/2147/ for crystallographic files in .cif format.

Discussion

The structure consists of one-dimensional polymeric cobalt hydrogenphosphate anions of formula $[Co(HPO_4)_2]^{2-}$ running parallel to the *a* axis. The Co^{2+} ions are tetrahedrally coordinated by four O atoms, which is consistent with the deep-blue colour of the compound. The Co–O bond lengths (average 1.952 Å) are similar to those observed in other cobalt phosphates, for example, in $[H_3N(CH_2)_2NH_3]_{0.5}[Co(PO_4)]$, $Co–O_{av}$ 1.95 Å.[11] The structure contains two crystallographically distinct HPO_4^{2-} ions. One of the P–O distances of each PO_4 tetrahedron is significantly longer than the other three (P(1)–O(1), 1.565(3) and P(2)–O(5), 1.584(3) Å), suggesting that these O atoms are protonated. The presence of hydroxyl groups was confirmed by the observation of peaks in Fourier-difference maps close to O(1) and O(5) corresponding to the H atom positions.

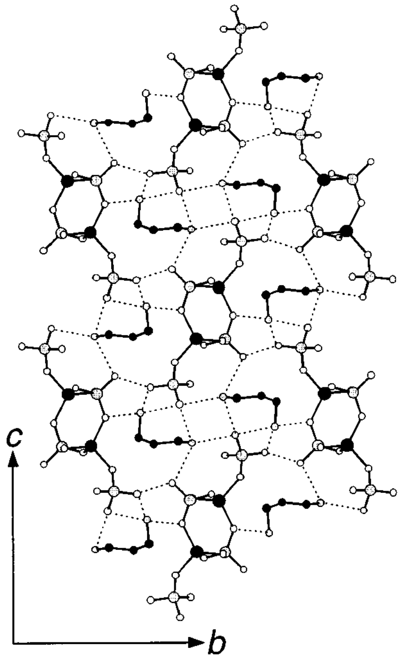

Fig. 3 View of the compound along the *a* axis showing the packing of $[Co(HPO_4)_2]^{2-}$ chains and charge-balancing $[H_3N(CH_2)_3NH_3]^{2+}$ cations. Inter-chain and amine–chain hydrogen bonds are shown as dotted lines. Hydrogen atoms have been omitted for clarity. Key: large black circles, Co; large grey circles, P; white circles, O; small grey circles, N, small black circles, C.

The CoO_4 and $HP(1)O_4$ units are linked alternately to form a zigzag "backbone" constructed from edge-sharing four-membered rings of tetrahedra (Fig. 2). The $HP(2)O_4$ group is bonded to these chains through only one bridging oxygen, O(6), to form "pendant" groups. In addition to the hydroxyl group, the pendant phosphorus carries two terminal oxygen atoms with P–O distances sufficiently short to suggest the presence of some degree of multiple bonding (P(2)–O(7) and P(2)–O(8), 1.521(3) Å). The hydroxyl groups of the pendant $HP(2)O_4$ units form *intra*-chain hydrogen bonds to bridging oxygen atoms of the backbone (O(5) ··· O(2) = 2.654(4) Å) (Fig. 2) whilst the hydroxyl groups of the backbone $HP(1)O_4$ units form *inter*-chain hydrogen bonds to P=O oxygens of the pendant $HP(2)O_4$ units (O(1) ··· O(8) = 2.455(4) Å) (Fig. 3). In order to balance the charge of the polymeric anion, the organic counterion must be diprotonated. Each NH_3 group forms three hydrogen bonds to O atoms of the anions (N ··· O distances in the range 2.790(5) to 2.963(4) Å), thus forming a 3-dimensional network of hydrogen bonds between chains.

Although this compound is the first reported example of a transition-metal phosphate containing this type of tetrahedron-based chain, similar one-dimensional structures have been observed previously in the two aluminophosphates $[C_{10}N_2H_9][Al(PO_4)(H_2PO_4)]$[13] and $[H_3N(CH_2)_2NH_3][Al(PO_4)(HPO_4)]$.[14] However, the chain packing and hydrogen-bonding schemes in the three materials are very different, there being no direct *inter*-chain hydrogen bonding in either of the aluminophosphates. Although the present compound contains the same organic amine as the layered cobalt phosphate $[H_3N(CH_2)_3NH_3]_{0.5}[Co(PO_4)]\cdot 0.5H_2O$,[5] there is no apparent structural relationship between the two materials. In contrast to the present compound, the layered material was prepared under aqueous conditions, illustrating the important role played by the solvent in directing framework formation in solvothermal syntheses.

Table 1 Crystallographic data for $[C_3N_2H_{12}][Co(HPO_4)_2]$

Molecular formula	$C_3H_{14}CoN_2O_8P_2$
Formula weight	327.03
T/K	150
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	5.210(1)
b/Å	12.693(1)
c/Å	15.518(1)
U/Å^3	1026.1
Z	4
μ/mm^{-1}	2.01
Unique data	2030
Observed data with $I > 3\sigma(I)$	1721
Merging R (%)	4.50
R (%)	3.24
R_w (%)	3.70

Table 2 Selected bond lengths (Å) and angles (°)

Co(1)–O(2)	1.980(3)	P(2)–O(5)	1.584(3)
Co(1)–O(3)	1.945(2)	P(2)–O(6)	1.510(3)
Co(1)–O(4)	1.950(3)	P(2)–O(7)	1.521(3)
Co(1)–O(6)	1.933(3)	P(2)–O(8)	1.521(3)
P(1)–O(1)	1.565(3)	N(1)–C(1)	1.495(5)
P(1)–O(2)	1.537(3)	N(2)–C(3)	1.492(5)
P(1)–O(3)	1.519(3)	C(1)–C(2)	1.519(5)
P(1)–O(4)	1.523(3)	C(2)–C(3)	1.508(6)
O(1)–H(1)	1.03(6)	O(5)–H(2)	0.82(6)
O(2)–Co(1)–O(3)	108.7(1)	O(5)–P(2)–O(6)	110.1(2)
O(2)–Co(1)–O(4)	117.6(1)	O(5)–P(2)–O(7)	104.5(2)
O(3)–Co(1)–O(4)	109.0(1)	O(6)–P(2)–O(7)	112.7(2)
O(2)–Co(1)–O(6)	101.3(1)	O(5)–P(2)–O(8)	107.5(2)
O(3)–Co(1)–O(6)	112.6(1)	O(6)–P(2)–O(8)	110.2(2)
O(4)–Co(1)–O(6)	107.5(1)	O(7)–P(2)–O(8)	111.6(2)
O(1)–P(1)–O(2)	105.8(2)	Co(1)–O(2)–P(1)	127.4(2)
O(1)–P(1)–O(3)	108.5(2)	Co(1)–O(3)–P(1)	129.0(1)
O(2)–P(1)–O(3)	111.7(1)	Co(1)–O(4)–P(1)	126.7(2)
O(1)–P(1)–O(4)	107.6(2)	Co(1)–O(6)–P(2)	140.2(2)
O(2)–P(1)–O(4)	111.4(2)	P(1)–O(1)–H(1)	113(3)
O(3)–P(1)–O(4)	111.5(2)	P(2)–O(5)–H(2)	114(4)
N(1)–C(1)–C(2)	110.2(3)	C(2)–C(3)–N(2)	111.5(3)
C(1)–C(2)–C(3)	112.6(3)		

One possible route to the synthesis of two- and three-dimensional open-framework phases is the use of low-dimensional metal-phosphate precursors which contain structural elements present in the desired higher-dimensional framework. Examples of syntheses of novel aluminophosphate frameworks by this method have previously been reported. For example the unidimensional material $[C_5H_9NH_3]_5[Al_3(PO_4)_4(HPO_4)]$ undergoes conversion into the layered phase $[C_5H_9NH_3]_2[Al_2(PO_4)_2(HPO_4)]$ on thermal treatment at 473K.[15] The unidimensional cobalt hydrogenphosphate reported in this work may have potential utility in this role because the chain of edge-sharing four-membered rings which forms the "backbone" of the structure occurs as a structural element in many zeolite frameworks, *e.g.* gismondine and chabazite. Loss of the pendant phosphate groups and cross-linking of the chains might therefore result in formation of a 3-dimensional framework material. Work is in progress to study the effects of thermal treatment on the compound.

Acknowledgements

A. R. C. would like to thank the Engineering and Physical Sciences Research Council for a studentship.

References

1 S. Natarajan, J.-C. P. Gabrial and A. K. Cheetham, *Chem. Commun.*, 1996, 1415.
2 V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta, C. J. O'Connor and Y.-S. Lee, *Chem. Mater.*, 1993, **5**, 1690.
3 K.-H. Lii and Y.-F. Huang, *Chem. Commun.*, 1997, 839.
4 D. Riou and G. Férey, *J. Solid State Chem.*, 1995, **120**, 137.
5 J. R. D. DeBord, R. C. Haushalter and J. Zubieta, *J. Solid State Chem.*, 1996, **125**, 270.
6 T. Loiseau, F. Serpaggi and G. Férey, *Chem. Commun.*, 1997, 1093.
7 S. Kamoun, A. Jouini and A. Daoud, *Acta Crystallogr., Sect. C*, 1991, **47**, 117.
8 Z. Otwinowski and W. Minor, *Methods Enzymol.* 1997, 276.
9 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 453.
10 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, *CRYSTALS User Guide*, Chemical Crystallography Laboratory, University of Oxford, 1996.
11 J. Chen, R. H. Jones, S. Natarajan, M. B. Hursthouse and J. M. Thomas, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 639.
12 ATOMS for Windows v3. 1, Shape Software, Kingsport, TN, 1997.
13 A. M. Chippindale and C. Turner, *J. Solid State Chem.*, 1997, **128**, 318.
14 I. D. Williams, J. Yu, Q. Gao, J. Chen and R. Xu, *Chem. Commun.*, 1997, 1273.
15 S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Chem. Mater.*, 1996, **8**, 2391.

Paper 9/01469A